MI/DNRE/WB-10/021

MICHIGAN DEPARTMENT OF NATURAL RESOURCES AND ENVIRONMENT
SURFACE WATER ASSESSMENT SECTION
WATER BUREAU
July, 2010

STAFF REPORT

2009 SELENIUM MONITORING CONDUCTED BY SELENIUM MONITORING WORK GROUP AROUND EMPIRE AND TILDEN MINES MARQUETTE COUNTY, MICHIGAN JULY 2010

Introduction

Cliffs Natural Resources (CNR) operates the Empire and Tilden mining facilities in the Marquette Iron Range near the town of Palmer (Marquette County). The Empire Mine has operated since 1963, while the Tilden Mine began operations in 1974. Because of concerns about selenium (Se) detections in facility effluents, waste rock seeps, and nearby surface waters, the Michigan Department of Natural Resources and Environmental (MDNRE) formed an internal work group in 2008 to: 1) assess Se levels and the extent and severity of associated water quality impacts; 2) determine whether additional monitoring is warranted; and 3) identify any needed facility permit modifications. A detailed description of the area, as well as a review of selenium characteristics, toxicity, and sources, is provided in a previous report (MDEQ 2009). The work group consisted of the following MDNRE, Water Bureau staff: Steve Casey, William Dimond, Gary Kohlhepp, Alvin Lam, William Taft, and Ben Thierry. It also included Doug Knauer and George Pelkola, both contract staff.

The work group conducted extensive water quality monitoring in 2008 to identify waters where Se levels were elevated and may be impacting chemical and/or biological integrity. Water and sediment were collected and analyzed at 20 primary sites and a few secondary sites in the vicinity of Tilden and Empire Mines. Fish and benthic macroinvertebrate tissue samples also were collected and analyzed from selected locations. The 2008 results indicated elevated selenium levels in some waterbodies, especially Warner Creek, Goose Lake Inlet, and Goose Lake (MDEQ 2009).

As described in the initial monitoring plan, the workgroup recognized that a second stage of monitoring likely would be needed to further assess potential problem areas identified in the first sampling stage and document the extent and severity of Se impacts on affected waters. That was the purpose of the monitoring conducted in 2009, and the results are summarized in this report.

In addition to the DNRE efforts, CNR conducted extensive monitoring at and around the Empire and Tilden Mines in 2009. Those results will be summarized in separate reports issued by CNR, and are not included in this report.

Methods

Study Design and Site Selection

The 2008 water, sediment, and fish tissue results were used as the basis for selecting the 2009 sampling locations. The workgroup identified three primary objectives for the 2009 monitoring:

1. Determine the geographic extent of elevated selenium levels in fish tissues;
2. Evaluate selenium concentrations in water and sediment at/around historic, inactive mines; and
3. Measure temperature and dissolved oxygen (DO) levels in Goose Lake, to assess whether low dissolved oxygen levels could be responsible for fish kills observed in previous years.

The 2008 data indicated elevated fish tissue Se concentrations from Warner Creek and Goose Lake Outlet, while high concentrations in water and sediment were documented at these and other sites (MDEQ 2009). Thus, our first objective for 2009 was to more precisely define the area and associated waterbodies with elevated Se in fish tissues. To do this, four locations were selected for fish tissue collection and analysis: East Branch Escanaba River (west of Sawyer); Green Creek (@ MQ Road); Ely Creek; and the Mary Charlotte Outlet (@ the railroad crossing). These sites represented previously unsampled waters adjacent to the mines or were downstream from 2008 sites found to have high Se concentrations.

The second objective was meant to establish whether elevated Se is a common occurrence at mines with large waste rock piles. Two historic mines in Marquette County, Republic Mine and Groveland Mine, were selected for this purpose. Specific sampling sites for the Republic Mine included the mine pit, the outlet, a nearby site on the Michigamme River, and a seep at the base of a waste rock pile. Groveland Mine locations included below the tailings pond, the headwaters of Pine Creek, an old water system intake, and the West Branch of the Sturgeon River.

To address the third objective, temperature and dissolved oxygen profiles were taken at two sites in the middle of Goose Lake. These profiles were taken in the early morning on August 13, 2009, prior to sunrise. The intent was to capture the time period when dissolved oxygen levels would be at a minimum.

Sampling Procedures

Water Collection

Water samples were collected in 16 ounce (473 milliliter [mL]) high density polyethylene bottles. In streams, the water samples were collected upstream of the collector while using latex powder-free disposable gloves. Ten drops of H_2SO_4 per bottle were added as a preservative for Kjeldahl-N, NO_3 + NO_2-N, NH_4-N, total phosphorus, and total organic carbon. In a second bottle, 5 mL of HNO_3 per bottle was added as a preservative for total metals. No preservative was added to a third bottle for pH, conductance, and SO_4. In most cases, the water samples were shipped on ice the day of collection by overnight courier to the MDNRE, Environmental Laboratory, in Lansing.

In Goose Lake, depth profiles of temperature and dissolved oxygen were taken using a YSI Model 57 dissolved oxygen/temperature meter.

Sediment Collection

The MDNRE staff sampled organic sediments at selected locations at or near the historic Republic Mine and Groveland Mine. Sediments were collected using a glass or plastic jar to scoop the sediments and place them in a stainless steel bowl. Each composite sample was thoroughly mixed and put into a glass jar with a Teflon cap liner and kept refrigerated until it was shipped on ice to the MDNRE, Environmental Laboratory, in Lansing.

Fish Tissue Collection

On July 20-21, 2009, MDNRE staff collected fish at four locations, specifically the East Branch Escanaba River, Green Creek, Ely Creek, and the Mary Charlotte Drainage. The MDNRE staff selected a downstream entry point at each location to collect fish for tissue analysis and followed the fish collection procedures outlined in the Surface Water Assessment Section Procedure 51 (MDEQ, 1990). A backpack shocking unit was used and adjusted to the local water conductivity conditions for maximum performance. Fish sampling proceeded by wading in an upstream direction and all fish were collected in five gallon plastic buckets. The time of collection, along with average stream width and depth measurements, was recorded.

All fish samples for tissue analysis were put in plastic bags, placed on ice, and transported to the Michigan Department of Community Health, Analytical Chemistry Laboratory (MDCH-AC) in Lansing, where they were frozen. Fish were identified to species, and fish weight and length (in larger individuals) were recorded.

Analytical Procedures

All water and sediment samples collected during this study were analyzed by the MDNRE, Environmental Laboratory, in Lansing. Se in water samples was analyzed by Inductively Coupled Plasma-Mass Spectrometry following United States Environmental Protection Agency (USEPA) Method 200.8. Se in sediment was analyzed according to USEPA Method 6020A. Samples were also analyzed for a suite of other parameters using USEPA-approved methods. All water samples are reported as unfiltered total Se and all sediment results are reported as dry weight.

Fish tissue samples were prepared for laboratory analysis and analyzed as individual whole samples if a minimum of 2 grams of tissue was available. Smaller fish were randomly divided into composite samples of whole fish.

Fish samples were delivered to the MDCH-AC for analysis of Se content. The MDCH-AC followed standard operating procedures for tissue homogenization prior to analyzing the samples for Se using techniques based on USEPA Method 200.11. All fish tissues were analyzed as wet weight. Analytical results were reported to the MDNRE electronically and were added to the Fish Contaminant Monitoring database.

Fish Tissue

Fish were collected on July 20-21, 2009, for analysis of whole-body Se concentrations, with all tissue results reported as wet weight (Table 3). Among the four stations monitored in 2009, the highest Se levels occurred at the Mary Charlotte Outlet. Mean Se levels at that site ranged from 10.5 to 16.4 parts per million (ppm) in the tissues of white suckers, fathead minnows, and pearl dace (Table 3). Mean concentration was greatest in pearl dace and lowest in white sucker.

Fish tissue Se levels were generally similar at the other three locations, with perhaps slightly higher levels at the East Branch Escanaba River station than at the Green Creek and Ely Creek locations (Table 3). In addition, fish tissue Se concentrations at all four stations sampled in 2009 were several times higher than Se levels in fish from sites further downstream, including Bear Creek and the East Branch Escanaba River near Gwinn (both sampled in 2008; Figure 1).

Because the 2009 fish tissue results are reported as wet weight while the draft USEPA fish selenium criterion is dry weight, the 2009 data must be multiplied by a factor based on the moisture percentage in the tissues. The moisture content was determined for selected ground and homogenized tissue samples by weighing the samples before and after drying (48 hours at 90 degrees C) in May 2009. The wet weight concentrations should be multiplied by a factor of four to calculate the corresponding dry weight concentration (Table 4; MDEQ 2009).

In addition to the whole fish samples, fish tissue fillets collected from Goose Lake and Schweitzer Reservoir in 2009 were analyzed for Se content. Elevated levels were found in northern pike (9.5 ppm) and sucker (11.7 ppm) fillets from Goose Lake, while levels in northern pike (2.0 ppm) from Schweitzer Reservoir were much lower (Figure 1).

Water and Sediment

One water sample was collected from each of four locations in and around both the Republic and Groveland Mines, both inactive and in Marquette County. The four Republic Mine water samples were collected on June 17, 2009, while the four Groveland samples were collected on June 25, 2009. Se concentrations of all eight samples were below the quantification level (1 ug/L; Table 4). Two of the four sites at each mine were re-sampled on September 2, 2009; concentrations of Se of all four of these water samples also were below the detection level.

Sediment samples were collected on September 2, 2009, from two locations at the Republic Mine and two locations at Groveland Mine (Table 4). Se concentrations were low (i.e. < 2 mg/kg) in samples collected at three of the sites. The exception was the sediment sample at the Republic Mine Pit, in which the Se concentration was moderately elevated (7 mg/kg).

Goose Lake Temperature and Dissolved Oxygen

Early morning, pre-sunrise profiles were taken at two locations near the center of Goose Lake on August 13, 2009 (Table 5). The maximum temperature at both locations was 22.8 degrees Celsius (C), while the minimum temperature was 20 degrees C at the first site and 19.5 degrees C at the second. These temperatures are similar to the 21.9 degrees C measured in Goose Lake down to a depth of 4.5 meters on July 10, 2008 (MDEQ 2009).

The DO ranged from 11-11.2 mg/L from the surface down to four meters at the first Goose Lake location, before dropping to 2.1 mg/L at five meters, near the bottom (Table 5). Similarly, DO ranged from 11.2-11.4 from the surface to three meters at the second site, before gradually dropping to a low of 2 mg/L near the bottom. The DO levels in the first few meters of depth at both locations were higher than the 8.3-8.6 mg/L found in Goose Lake on July 10, 2008.

Discussion

When considering potential Se impacts on aquatic life and associated wildlife, fish tissue is considered the best risk indicator (USEPA, 2004). If Se is not elevated in representative fish tissue, adverse effects are unlikely. Because of the bioaccumulative nature of Se toxicity, the

USEPA (2004) has drafted a water quality value of 7.91 mg/kg in fish tissue (**dry weight**, whole body). Fish tissue measurements in 2009 reinforce the 2008 fish and benthic macroinvertebrate tissue data indicating that Se is accumulating at levels that may have adverse impacts on aquatic life. Wet weight mean tissue Se concentrations of all fish species sampled from the Mary Charlotte Drainage exceeded the USEPA draft water quality value, even prior to conversion to dry weight (Figure 1, Table 3). Mean Se concentrations in all species from the other three locations monitored in 2009 exceeded the USEPA value after conversion to dry weight (Table 3).

All fish tissue results (wet weight) generated in 2008 and 2009 are shown in Figure 1. After conversion to dry weight values, mean Se levels in all analyzed fish species at every site near the Empire and Tilden Mines exceed the proposed USEPA criteria (i.e. mean wet weight Se concentration in samples from all species were > 2 ppm). In contrast, Se levels were low in fish tissue samples from Bear Creek (a control site) and the East Branch Escanaba River in Gwinn (well downstream of the CNR mining facilities). Even with a wet weight/dry weight conversion, fish from these two waterbodies were below the draft criterion. These results suggest elevated Se levels are ubiquitous in fish (and benthic macroinvertebrates, per 2008 data) from waters immediately surrounding the facilities, with runoff/discharge from the mines being the likely Se source.

Water samples were collected from several sites at/near the historic Republic and Groveland Mines in 2009, to determine whether elevated Se levels in water are common due to local geology and/or as by-product of mining operations. Se concentrations in all 12 water samples were below the quantification level (i.e. <1 ug/L). Of the 75 water samples in/around the Empire and Tilden Mines analyzed in 2008, Se concentrations of 39 samples (52 percent) were below detection. Taken together, these results suggest that elevated Se levels are not “typical” for waterbodies in Marquette County, and that in those waters that do have elevated Se concentrations, a local source is likely. The 2008 data showed Michigan Water Quality Standard exceedances (5 ug/L, chronic aquatic life) in Warner Creek, Goose Lake Inlet, Mary Charlotte Outlet, and Partridge Creek. All are in waters influenced by CNR mining operations.

Water is often a key transport medium for the soluble Se forms. However, sediments represent a major Se sink for insoluble and organic forms, and therefore, a potential perennial source for bioaccumulation of Se by aquatic and terrestrial life (Lemly, 1997). Because of the propensity of Se to accumulate in sediment, sediment Se concentrations may be elevated when water Se concentrations are very low, even below a level of quantitation (Lemly, 2002).

A maximum 2 mg/kg Se sediment concentration has been recommended in literature (Lemly, 2002) to protect against bioaccumulative chronic toxicity risk in aquatic life and other water-dependent biota. In addition, Lemly characterizes sediment Se concentrations >4 mg/kg as having a high risk of bioaccumulative toxicity. Of the four historic mine sites sampled for sediment, three had sediment Se levels below 2 mg/kg. However, sediment Se concentration at a Republic Mine pond, at 7 mg/kg, was above Lemly’s high risk level. Of the 19 streams, rivers, and lakes from which sediments were analyzed in 2008, only two (Goose Lake and Warner Creek) had greater Se concentrations than the Republic Mine pond (MDEQ 2009). Se concentrations in water and fish tissues are elevated around Empire and Tilden Mines compared to other locations. Sediment levels around Empire and Tilden Mines are also elevated compared to three of four samples from historical mines. The fourth sample, a pond at Republic Mine, appears to be comparable to results from the vicinity of the Empire and Tilden Mines.

Fish kills have been observed in Goose Lake in previous years. Because of its eutrophic condition and shallow depth, it is believed that periodic anoxic (or near anoxic) conditions are the cause of the fish kills. A draft TMDL, currently out for public comment, proposes a phosphorus reduction goal (summer monthly average concentration of 0.030 mg/L) in Goose Lake to eliminate the nuisance algae blooms, fish kills, and odor problems. Dissolved oxygen profiles conducted in 2008 and 2009 found sufficient oxygen levels (> 8.3 mg/L) to support a warmwater fish community. However, these results do not rule out the occurrence of periodic low DO conditions in some years. In addition, it should be noted that Michigan experienced a cool summer during 2009, and algal growth in August 2009 was observed to be less than normal (Knauer and Pelkola, pers. comm.).

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Tables

Table 1. Fish contaminant site locations.

Site	Location	GPS Coordinates
East Branch Escanaba River	West of Sawyer	46.36691, -87.45348
Green Creek	MQ Road	46.3563, -87.57547
Ely Creek		46.44725, -87.68451
Mary Charlotte Outlet	Railroad crossing	46.48008, -87.56302

Table 2. Historic mine water and sediment sampling locations.

Site	GPS Coordinates
Republic Mine Pond	46.39810, -87.96552
Republic Mine Outlet	46.40433, -87.98114
Michigamme River near Republic Mine	46.39819, -87.98772
Republic Mine Waste Rock Seep	46.38351, -87.97505
Groveland Mine below the tailings pond	45.97181, -87.98056
Pine Creek headwaters near Groveland Mine	45.94804, -87.98313
Old water system intake near Groveland Mine	45.97430, -87.98865
West Branch Sturgeon River	46.01323, -87.97992

Table 3. Whole fish mean selenium concentrations, July 2009 (ppm wet weight). Values in parentheses are estimated dry weight concentrations, based on a conversion factor of four (MDEQ 2009).

Waterbody	Brook Trout	White Sucker	Creek Chub	Fathead Minnow	Pearl Dace	Blacknose Dace
East Branch Escanaba R	5.7 (22.8)	4.7 (18.8)	3.0 (12)	3.9 (15.6)		4.7 (18.8)
Green Creek	4.5 (18)	3.0 (12)	4.2 (16.8)		3.4 (13.6)	3.9 (15.6)
Ely Creek	4.1 (16.4)	2.1 (8.4)	2.3 (9.2)		3.7 (14.8)	
Mary Charlotte Outlet		10.5 (42)		12.5 (50)	16.4 (65.6)	

Table 4. Water and sediment selenium concentrations at the historic Republic and Groveland Mines, Marquette County.

Location	June 2009	September 2009	
	Water (ug/L)	Water (ug/L)	Sediment (mg/kg)
Republic Mine Pond	Non-detect	Non-detect	7.0
Republic Mine Outlet	Non-detect		
Republic Mine Waste Rock Seep	Non-detect	Non-detect	1.7
Michigamme River near Republic Mine	Non-detect		
Groveland Mine below the tailings pond	Non-detect	Non-detect	0.78
Pine Creek headwaters near Groveland Mine	Non-detect	Non-detect	0.85
Old intake site near Groveland Mine	Non-detect		
Sturgeon River near Groveland Mine	Non-detect		

Table 5. Goose Lake temperature and dissolved oxygen profiles, August 13, 2009.

	Location 1		Location 2	
Depth (m)	Temperature ^{0}C	DO (mg/L)	Temperature ^{0}C	DO (mg/L)
Surface	22.8	11.2	22.8	11.4
1	22.8	11.0	22.8	11.2
2	22.8	11.2	22.8	11.2
3	22.0	11.2	22.0	11.2
4	21.8	11.0	20.8	6.6
5	20.0	2.1	19.5	3.4
5.5			19.5	2.0